RESTRICTED ROTATION IN *Beta*-SUBSTITUTED ACRYLIC ACIDS

BY

RALPH SEYMOUR LUDINGTON

B.Chem., Cornell University, 1940
Chem.E., Cornell University, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1944

URBANA, ILLINOIS
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Following the prediction of Hyde and Adams[1] of optical activity in hindered arylolefins, a number of compounds of this type were synthesized and their resolution effected. On the basis of this work, attempts have been made to determine the minimum amount of hindrance necessary for optical activity, and to predict the relative stability of the active compounds. The purpose of this investigation was to test some of these predictions and to obtain experimental evidence upon which future generalizations could be based.

Discussion of Results

Adams and Theobold[2] prepared β-methoxy-β-(2,4,6-trimethyl-3-bromophenyl)-acrylic acid and hypothesized a *trans* configuration to explain their failure to effect a resolution. On the basis of this explanation, α-methyl-β-methoxy-β-(2,4,6-trimethyl-3-bromophenyl)-acrylic acid should be capable of resolution. This acid was prepared by the action of diazomethane on α-methyl-2,4,6-trimethyl-3-bromobenzoyl acetic acid, and subsequent hydrolysis of the methyl α-methyl-β-methoxy-β-(2,4,6-trimethyl-3-bromophenyl)-acrylate formed. Resolution could not be effected by means of either the brucine or the quinine salts.

β-Substituted β-(2,4-dimethyl-3-chloro-6-methoxyphenyl)-acrylic acids were prepared in which the β-substituents were chlorine, bromine, iodine, methylthio, and methoxy. The chlorine compound was found to be identical with the acid prepared by Adams and Gross[3] by a different method. The bromine compound was resolved by means of the quinine salt; *d*-β-bromo-β-(2,4-dimethyl-3-chloro-6-methoxyphenyl)-acrylic acid was found to have a specific rotation at 28° of 34.7° and a half-life of 250 minutes (28°), 420 minutes (20°). The iodine compound was found to be unstable in the presence of alkaloid bases, and the attempt at resolution had to be abandoned. The methylthio compound could not be resolved by means of either the brucine or the quinine salts. The methoxy compound could not be resolved by means of the quinine salt.

Degradation of the bromo- and iodoacrylic acids gave no information as to the configuration of the acids since the condi-

tions necessary for the reaction were vigorous enough to allow isomerization. When heated under reflux with a mixture of constant-boiling hydriodic and glacial acetic acids, both β-iodo- and β-bromo-β-(2,4-dimethyl-3-chloro-6-methoxyphenyl)-acrylic acids were transformed into 4-iodo-5,7-dimethyl-6-chlorocoumarin. Similarly, β-bromo-β-(2,4-dimethyl-3-chloro-6-methoxyphenyl)-acrylic acid was converted into 4-bromo-5,7-dimethyl-6-chlorocoumarin after heating under reflux for four hours in the presence of constant-boiling hydrobromic acid and glacial acetic acid.

Bibliography

[1] Hyde and Adams, J. Am. Chem. Soc. **50,** 2499 (1928).
[2] Adams and Theobold, ibid. **65,** 2383 (1943).
[3] Adams and Gross, ibid. **64,** 1786 (1942).

Vita

The writer was born on December 23, 1919, near Holley, New York. He received his early education in the public schools in and near that village, and in 1936 was graduated from Holley High School. In September, 1936, he entered Cornell University, and was graduated in 1940 with the degree of Bachelor of Chemistry and in 1941 with the degree of Chemical Engineer.

In 1941, he enrolled in the Graduate School of the University of Illinois. He held the position of Assistant in Chemistry during the year 1941-42; he was awarded a University Fellowship for the year 1942-43 and the Allied Chemical and Dye Corporation Fellowship for the year 1943-44.

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